SCIENCE FOR CERAMIC PRODUCTION

UDC 666.762.1/.14-134

CHEMICAL RESISTANCE OF CERAMIC MATERIALS IN ACIDS AND ALKALIS

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Translated from Steklo i Keramika, No. 10, pp. 22 – 24, October, 2004.

A method for determining the acid and alkali resistance of ceramic materials has been developed and certified. Numerical values of acid and alkali resistance of different materials and powders has been determined using a unified method. The possibility of designing chemically resistant ceramic materials with prescribed numerical values of acid an alkali resistance is demonstrated.

The surface of products made of ceramics, as a rule, is subjected to a corrosive effect of the ambient medium. It may be either chemical reactions between the ceramic material components and the ambient medium elements, or their dissolution in the ambient medium volume.

Usually mutual diffusion of ions (atoms) of ceramics and an aggressive medium takes place in corrosion. The diffusion is not necessarily accompanied by the destruction of the material, but its properties are modified to such an extent that its subsequent service in the particular structure becomes impossible.

Corrosion is discriminated depending on the type of the medium affecting a product. Corrosion can be gaseous (inert or chemically active gases) or liquid (solutions of acids, bases, salts; melts of salts, glasses, slag, metals; sea and fresh water, etc.). The factors influencing the corrosion resistance of materials are divided into internal (thermodynamic resistance, state of the surface, structure and composition) and external (medium temperature, aggressive medium flow velocity; ratio between the aggressive medium volume and the material surface, composition of aggressive medium, etc.).

Chemical resistance of ceramics is understood as its capacity to withstand a destructive action of aggressive media. Chemical resistance depends on the properties of the corrosive medium, the chemical composition and microstructure of ceramics, and the conditions of the corrosion process, especially in the site of the contact of ceramics with the aggressive medium. Two main types of chemical resistance of ceramics are distinguished: acid and alkali resistance.

The study of corrosion resistance of ceramics in acid and alkalis makes it possible to predict their service properties in these media. The literature contains numerous data on the resistance of ceramics in acids, however, the data on the resistance of ceramics in alkalis are scarce. Thus, data on chemical resistance of silicon carbide and aluminum oxide ceramics in different acids and alkalis are given in [1] (Table 1).

It can be seen that corrosion resistance is estimated based on weight losses.

A booklet of the Friedrichfeld Company (Germany) give data on the chemical resistance of ceramic materials with 96.0 and 99.5%[2] Al_2O_3 in various acids and alkalis. Chemical resistance is estimated based on the weight loss parameter: from 0.015 to 150 mm/year. The chemical resistance of corundum ceramics in acids and alkalis is shown in Table 2.

The authors in [2] determined the corrosion resistance of sintered corundum by boiling a fragment of finished product

TABLE 1

Reactant	Mass content, %	Treatment temperature, °C	Weight loss, mg/(cm^2 · year)		
			recrystallized SiC	self-bound SiC (12 wt.% Si)	densely sintered Al_2O_3 (99 wt.% Al_2O_3)
H_2SO_4	98	100	1.8	55.0	65.0
HNO_3	70	100	< 0.2	0.5	7.0
H_3PO_4	85	100	< 0.2	8.8	< 1000
HCl	25	70	< 0.2	0.9	72.0
HF	53	25	< 0.2	7.9	20.0
HF + HNO_3	10 + 57	25	< 0.2	< 1000	16.0
NaOH	50	100	2.5	< 1000	75.0
KOH	45	100	< 0.2	< 1000	6.0

[1] Bakor Scientific Technical Center, Russia.

[2] Here and elsewhere in wt.%.

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TABLE 2

Reactant	Mass content, %	Treatment temperature, °C	Corrosion, mm/year, of corundum ceramics, less than	
			Frialit F-96 (96.0% Al_2O_3)	Frialit F-99.7 (99.5% Al_2O_3)
H_2SO_4	97	105	0.110	0.120
HNO_3	65	105	0.030	0.040
H_3PO_4	105	105	0.090	0.095
HCl	35	105	0.018	0.020
HF	40	20	0.450	0.100
$C_6H_8O_7$	25	105	0.010	0.014
CH_3COOH	98	105	0.011	0.010
HCOOH	98	105	0.048	0.050
NaOH	40	105	0.150	0.040

TABLE 3

Reactant	Mass content, %	Weight losses, %, in boiling (100°C) of sintered corundum			
		without glass	containing high-alumina glass, %		
			0.5	1.0	2.0
HCl	40	0.010	0.013	0.015	0.023
HF	40	0.008	0.014	0.160	0.190
NaF	20	0.006	0.010	0.011	0.013

in a chemical reactant and estimated it based on the weight loss (Table 3).

It can be seen that the data on chemical resistance of ceramics supplied by particular authors are hard and sometimes impossible to correlate with results obtained by other authors. This is due to the fact that researchers use different measurement methods and, accordingly, obtain results that are impossible to compare.

At the same time, it should be noted that progress in science and engineering provides a topical challenge: development of ceramics with prescribed chemical resistance. At present this problem becomes even more complicated: not just ceramic materials with particular acid and alkali resistance values are required, but materials with high chemical resistance in regarding both parameters, i.e., high acid and alkali resistance.

Consequently, the main purpose of our study was to apply a unified generally accepted measurement method to obtain numerical values of acid and alkali resistance of the most common ceramic powders used in production of various ceramics. Standards GOST 473.1–81 and GOST 473.2–81 "Chemically resistant and heat-resistant ceramic products. The method for determining acid and alkali resistance" were selected as the basis for the measurement method. Based on these standards the Bakor Research and Production Center has developed measurement methods MI 11773998-1-2004 and MI 11773998-2-2004 (methods for measuring acid and alkali resistance of ceramic products) and implemented them in practice.

To verify the reliability of obtained results, the acid and alkali resistance of the same ceramic sample was measured at the Bakor Research Center and the Central laboratory of the Shchekinskii Works[3] of Acid-Resistant Materials using the same measurement method. The difference in the values of acid and alkali resistance of ceramic samples obtained in different laboratories did not exceed ± 0.1%.

The method for determining chemical resistance used in this work is based on determining the ratio of the weight of a milled ceramic article (powder) after its treatment in alkali (acid) to the weight of the same article (powder) before its treatment in alkali (acid). The weight of the sample taken was always 1.0000 g; the particle size of milled material (powder) was from < 1.0 to > 0.8 mm; the concentration of H_2SO_4 was 98%, NaOH was 35% aqueous solution; the powder together with the chemical reactant was boiled in a flask with a reverse cooler for 1 h. In determining the chemical resistance of ceramics all equipment has metrological certificates, which guarantees the reliability of parameters measured.

Table 4 shows the results of determining the chemical resistance of various ceramic powders used to produce ceramics.

Based on the data in Table 4, it can be inferred that to obtain ceramics able to successfully operate alternately in acid and alkali media (for instance, filtering elements) it is neces-

TABLE 4

Material	Reference standard	Weight losses, % in determining	
		acid resistance	alkali resistance
Electromelted corundum	TU 3988-064-00224450–94	99.79	99.99
Electromelted periclase	TU 14-8-448–83	52.87	97.55
Electromelted mullite	TU 14-8-450–83	98.53	98.23
Electromelted zirconium dioxide	TU 48-4-489–87	83.54	99.99
Melted quartz (99.9% SiO_2)	TU 14-8-487–85	99.27	82.27
Silicon carbide	GOST 3647–80	99.99	98.62

[3] The authors acknowledge the assistance of the team of the Central laboratory at the Shchekinskii Acid-Resistant Materials Works in studies performed.

TABLE 5

Material	Weight losses, %, in determining	
	acid resistance	alkali resistance
Polycor (99.5% α-Al_2O_3)	97.67	99.99
Microlit (99.8% α-Al_2O_3)	97.82	99.17
Self-bound silicon carbide (12% fixed Si)	99.99	87.80
Silicon nitride (hot-pressed)	99.32	88.59

TABLE 6

Parameter	Chemical resistance, %, of porcelain mixtures containing oxides, %					
	No. 1		No. 2		No. 3	
	SiO_2 67.00	Al_2O_3 23.00	SiO_2 56.60	Al_2O_3 38.32	SiO_2 25.00	Al_2O_3 71.00
Acid resistance	98.30		98.72		98.94	
Alkali resistance	58.12		72.19		88.59	

sary to take initial components which after sintering produce a maximum possible content either of α-Al_2O_3 (corundum), or $3Al_2O_3 \cdot 2SiO_2$ (mullite). Only these two materials among all materials tested have high values of acid and alkali resistance.

To verify the data obtained, the chemical resistance of several ceramic and porcelain materials was determined (Tables 5 and 6).

Thus, a method for determining acid and alkali resistance of ceramics has been developed and certified. Numerical values of acid and alkali resistance of various ceramic materials and powders have been determined. The possibility of designing chemically resistant ceramics with preset numerical values of acid and alkali resistance is demonstrated.

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